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# Anion-conducting ionomers: Study of type of functionalizing amine and macromolecular cross-linking

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## ABSTRACT

Anion exchange membranes (AEM) were prepared by chloromethylation and amination of polysulfone (PSU) and polyphenylsulfone (PPSU). The reaction pathways were studied by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and *ab-initio* calculations. Various amines were used, including trimethylamine (TMA), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,4-diazabicyclo[2.2.2]octane (DABCO) to study the influence of the molecular volume and the stabilizing effect of a delocalization of the positive ammonium ion charge on a second nitrogen. Furthermore, the effect of a solvothermal cross-linking on the stability of AEM was investigated. The alkaline stability, measured after treatment in 2 M KOH at 60 °C during 168 h, is improved by DBN and polymer reticulation. The ionic conductivity in water reaches values above 10 mS/cm with DABCO. The hydroxide ion mobility depends linearly on the hydration number.

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## Introduction

Anion exchange membranes (AEM) are very versatile ion-conducting materials used in several applications, such as alkaline fuel cells [1,2], water electrolyzers [3], redox flow batteries [4,5], or electrodialysis devices [6,7]. Many fields can benefit from their application: in alkaline fuel cells, which do not need noble metal catalysts, they reduce problems related to carbonation [8], while in redox flow batteries AEM achieve very low permeability and high selectivity [9].

AEM are formed by a polymeric backbone functionalized with fixed cationic groups and counter anions, generally hydroxide ions that sustain the conductivity. Anion

conductivities are lower than proton conductivities, but similar dependencies on humidity and temperature have been reported [10–12].

The stability in severe basic conditions and the reduced conductivity are the main problems of AEM to be solved in order to extend the use of these promising materials. Often the two issues are linked to each other, like in cation exchange membranes: high stability is related to low conductivity and vice versa [13,14].

The AEM stability can be discussed in terms of cationic groups and polymeric backbones. The backbone is responsible for the mechanical properties of membranes [15] and among different polymeric matrixes it was reported that the aromatic polymers polysulfones (PS), can well resist in basic conditions

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[16,17]. Aromatic polymers show many interesting properties: i) the possibility to tailor polymer structures by the use of various monomers or by functionalization; ii) an easy production and recycling of the corresponding membranes, with relatively little environmental pollution problems; iii) a low gas permeability; and iv) a low cost. In addition, PS are soluble in organic solvents, allowing homogeneous solution reactions, and present two activated positions per repeat unit towards electrophilic aromatic substitution, leading to high degrees of functionalization. Based on these considerations, polysulfone (PSU) and polyphenylsulfone (PPSU) seem to be a good choice as base polymers.

However, it was recently reported that trimethylammonium groups attached to PSU can catalyse the degradation of the polymer backbone by  $\text{OH}^-$  nucleophilic reaction on the quaternary carbon or on the ether junction. It was postulated that the cationic moieties can cause the formation of a dipole moment on the polymer backbone with a positive charge localized on the quaternary carbon or on the ether group facilitating the nucleophilic attack [18].

Regarding the stability of cationic groups, most used are ammonium ions because they show better chemical and thermal stability compared to other cationic groups, such as quaternary phosphonium and tertiary sulfonium ions [2]. However, ammonium groups present also several degradation reactions: bimolecular and unimolecular elimination ( $\text{E}_2$  and  $\text{E}_1$ ), bimolecular nucleophilic substitution ( $\text{S}_{\text{N}}2$ ), and ammonium ylide formation [19–21].  $\text{E}_2$  (often called Hofmann elimination) and  $\text{E}_1$  can be avoided using ammonium groups without  $\beta$ -hydrogens or, in the case of the Hofmann elimination reaction, using moieties where it is impossible to reach an anti-periplanar conformation; the substitution reaction and the ylide formation are more difficult to circumvent.

While the correlation between conductivity, ion exchange capacity (IEC) and stability seems clear in proton conducting polymers [22–24], this topic has been less studied in anionic membranes. High values of IEC lead to an increase of the water uptake and the conductivity, but also decrease the membrane processability by a microphase separation due to a polymer/polymer immiscibility according to Bauer et al. The formation of cross-linked backbones might help to avoid this phase separation [25]. Furthermore the presence of a covalent bond between the macromolecular chains can also decrease the degradation of the main chain due to the presence of ammonium ions [26]. We have reported the benefits of cross-linked (XL) polymers obtained by in situ reticulation [27–29]: thermal and mechanical stability are improved and also the conductivity [30,31]. The formation of cross-linked AEM (XL-AEM) is explored in this work.

Another option to decrease the degradation of cationic groups due to the  $\text{S}_{\text{N}}2$  reaction and the ylide formation is the reduction of the positive charge on the ammonium group by delocalization on different atoms. Furthermore, the performance of AEM may increase if these groups are more basic. To explore this possibility, we used 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,4-diazabicyclo[2.2.2]octane (DABCO) as quaternizing agents. Due to the presence of two nitrogens in these rings, the positive charge can be better stabilized making the polymer degradation more difficult.

This paper explores the influence of various functionalizing amines and of macromolecular cross-linking on the AEM properties and stability.

## Material and methods

### Materials

Polysulfone (Solvay, PSU, MW = 55,500) polyphenylsulfone (Solvay, PPSU, MW = 46,173), polyetheretherketone (Victrex, PEEK, 450 PF, MW = 38,300), stannic chloride ( $\text{SnCl}_4$ ), paraformaldehyde ( $(\text{CH}_2\text{O})_n$ ), trimethylchlorosilane ( $\text{Me}_3\text{SiCl}$ ), trimethylamine (TMA, 4.2 M in EtOH), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and all other chemicals (Aldrich) were reagent grade and were used as received.

### Synthesis of chloromethylated polymers

#### Chloromethylated-PSU (CMPSU)

a) Reagent ratio  $\text{PSU}:(\text{CH}_2\text{O})_n:\text{Me}_3\text{SiCl}:\text{SnCl}_4 = 10:100:100:1$ . After drying 2 h at  $80^\circ\text{C}$ , PSU (3.78 g, 8.55 mmol) was dissolved in chloroform (410 mL) at RT in a three-neck vessel equipped with a magnetic stirrer under nitrogen flux. The resulting solution was 0.021 M (concentration 2%). After dissolution, paraformaldehyde (2.57 g, 85.5 mmol) and trimethylchlorosilane (10.8 mL, 85.5 mmol) were added. Then  $\text{SnCl}_4$  (0.1 mL in 20 mL of chloroform) was slowly added to the solution with an addition funnel. The reaction was left under stirring at  $55^\circ\text{C}$  for 240 h. The solution was cooled to RT and then precipitated in ethanol. The product was dried overnight at  $60^\circ\text{C}$  and analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR using  $\text{CDCl}_3$  as a solvent. The final degree of chloromethylation (DCM) after 240 h was 0.86.

b) Reagent ratio  $\text{PSU}:(\text{CH}_2\text{O})_n:\text{Me}_3\text{SiCl}:\text{SnCl}_4 = 5:50:50:1$ . The initial procedure was the same reported above. After the first addition of the catalyst, the reaction was kept at  $55^\circ\text{C}$  for 24 h. Further 0.1 mL of  $\text{SnCl}_4$  diluted in 30 mL of chloroform were then added. The solution was kept at reflux for different times in order to obtain different degrees of chloromethylation as reported in Fig. 1. After the precipitation in ethanol, the products were analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR using  $\text{CDCl}_3$  as a solvent.

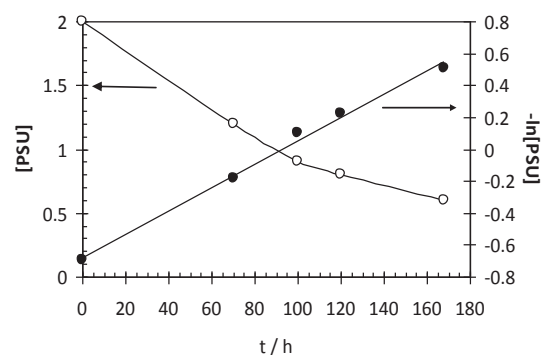


Fig. 1 – Concentration of unreacted PSU and logarithm of PSU concentration versus reaction time.

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